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Collision dynamics for an asymmetric top rotor and a linear rotor: coupled channel formalism and application to H_2O-H_2

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ABSTRACT

The close coupling formalism and the approximate coupled states formalism for collisions of an asymmetric top rigid rotor and a linear rigid rotor are reviewed. Calculations for excitation of H_2O by H_2 using a recent, accurate, ab initio potential energy surface are presented.

1. Introduction

Many physical phenomena can be described in terms of collision cross sections.[1] Some of these, of course, are adequately described by approximate methods involving averaged quantities and precise details of the molecular interactions and state-to-state cross sections are not required. However, detailed first-principles investigations are still desirable to put such approximate methods on a more secure theoretical basis and in order to provide the detailed results which are needed in some cases. Interpretation of radioastronomical observations of interstellar molecules is an application where detailed state-to-state collision rates are often required. It has generally not been possible to obtain these values experimentally but theoretical studies have proved very useful.[2] These molecules are often observed in regions where only a few rotational levels are populated, suggesting both the necessity and the possibility of accurate quantum coupled channel calculations. Of course, in addition to accurate molecular scattering calculations, accuracy of theoretical rates also depends on the verisimilitude of the interaction potential energy surface which is used.

Because the number of channels required for converged cross sections increases dramatically with the complexity of the collision partners, especially if both have internal degrees of freedom, most calculations to date have been limited to relatively simple systems in which one of the collision partners is a structureless atom. Although excitation by H_2 is the most important collisional mechanism in the interstellar gas, most studies have considered only excitation by He which is less abundant by a factor of four to five. With rapid increases in computational power, however, calculations are being extended to more complex systems, such as symmetric top rotors excited by diatomic molecules (NH_3-H_2)[3,4] and asymmetric top rotors excited by diatomic molecules (H_2O-H_2)[5].

The current effort is part of an ongoing study of interstellar water. This molecule is responsible for rather spectacular maser transitions observed in star-forming regions

and in the envelopes of some evolved stars[6] and is also thought to be important in the energy balance of these and other regions. Successively more refined calculations now appear to have provided converged values for excitation of H_2O by He.[7,8] We recently presented an extensive ab initio calculation for the interaction of H_2O-H_2, including a global fit.[9] We describe here initial molecular scattering calculations using this potential energy surface. The next section reviews the molecular scattering formalism and the following section presents studies of basis set convergence and tests of the accuracy of the coupled states approximation.

2. Molecular scattering formalism

This section describes the formalism for close coupling and approximate coupled states calculations for collisions of asymmetric rigid rotors with linear rigid rotors which has been implemented in the MOLSCAT[10] computer code and which differs slightly from that used in other studies.[3-5] We describe here our choice of coordinates, expansion basis functions, and functions used to expand the angular part of the intermolecular potential. We then give the resulting close coupling and approximate coupled states equations.

A. Coordinate systems

The collision is described in space-fixed coordinates placed at the center of mass of the two molecules to eliminate the translation of the system as whole. The collision coordinate, **R**, the vector from the asymmetric top center of mass to the linear rotor center of mass, is then conveniently described by spherical polar coordinates, R,Θ,Φ, where R is the radial distance, Θ is measured from the z-axis, and Φ is measured from the xz-plane. The orientation of the linear molecule can also be described with respect to this space-fixed coordinate by polar angles, Θ',Φ'. Three angles are required to describe the orientation of the asymmetric top with respect to the space-fixed axes,

traditionally the Euler angles α,β,γ which rotate the space-fixed axes to an axis system fixed in the frame of the molecule.

Following earlier work[11] we do not consider here the most general case, but assume that the asymmetric top has a plane of symmetry; this is always true for symmetric tops, such as NH_3, and is also true for H_2O. We choose the molecule-fixed axes such that the xz-plane is a plane of symmetry. If the molecule has a two-fold or higher axis of symmetry (always true for a symmetric top) we chose this axis as the molecule-fixed z-axis; otherwise (e.g., a planar molecule such as deuterated water) we choose one of the two principal axes of inertia which are in the molecular plane (the xz-plane) as the molecule-fixed z-axis. The molecular orientation $\alpha,\beta,\gamma = (0,0,0)$ then corresponds to alignment of the molecule-fixed and space-fixed axis systems. A general orientation α,β,γ is produced by rotating the molecule-fixed axis system, beginning at (0,0,0), by an angle α about the molecule-fixed z-axis, followed by a rotation β about the molecule-fixed y-axis, and then another rotation γ about the molecule-fixed z-axis.

B. Expansion basis functions

The wavefunctions for an asymmetric top rotor can be written as combinations of symmetric top eigenfunctions (rotation matrices),

$$W^{j}_{\tau,m}(\alpha\beta\gamma) = \sum_{k} a^{j}_{\tau,k} \, ([j]/8\pi^2)^{1/2} \, \mathscr{D}^{j}_{k,m}(\alpha\beta\gamma) \ , \qquad (1)$$

where the $\mathscr{D}^{j}_{k,m}$ are Wigner rotation matrices defined according to the conventions of Silver[12] and we use the notation $[j]=2j+1$; j is the total angular momentum of the rotor, m its projection on the space-fixed z-axis, k its projection on the molecule-fixed z-axis, and τ an index to distinguish the 2j+1 asymmetric top levels for each j. The coefficients $a^{j}_{\tau,k}$ may be obtained by diagonalizing the asymmetric top Hamiltonian,

$$\mathscr{H} = (2I_x)^{-1} \ \mathscr{J}_x^2 + (2I_y)^{-1} \ \mathscr{J}_y^2 + (2I_z) \ \mathscr{J}_z^2 \ , \qquad (2)$$

where I_α are the principal moments of inertia and $\mathscr{J}_\alpha$ the angular momentum operators

about the corresponding axes, in a symmetric top basis as discussed in Ref. 11 which gives the required matrix elements. As noted there, the moments of inertia *must* correspond to the rotor molecule-fixed coordinate system discussed above, and may differ in order from the standard spectroscopic A, B, C designation. The coefficients $a^j_{\tau,k}$ are real and have the properties

$$\sum_k a^j_{\tau,k} a^j_{\tau',k} = \delta_{\tau,\tau'} , \tag{3a}$$

$$a^j_{\tau,-k} = \varepsilon_{j,\tau} a^j_{\tau,k} , \tag{3b}$$

where $\varepsilon_{j,\tau}$ for a given j,τ is either plus or minus one. Further, for a given j,τ, $a^j_{\tau,k}$ are nonzero for only even or only odd k values; it will be convenient to describe this as

$$a^j_{\tau,k} = (1/2) [1 + (-1)^k \alpha_{j,\tau}] a^j_{\tau,k} , \tag{3c}$$

where $\alpha_{j,\tau}$ is either plus one, for even k, or minus one for odd k. Eq. (3a) is just a statement of the orthonormality of the asymmetric top wavefunctions. Eqs. (3b) and (3c) are a well known consequence of the fact that the asymmetric top wavefunctions transform according to irreducible representations of the D_2 space symmetry point group. Note that wavefunctions for a symmetric top rotor can be written as a special case of the asymmetric top expansion, Eq. (1). The wavefunctions for the linear rotor are spherical harmonics, $Y_{j,m}(\Theta',\Phi')$.

It is useful to construct expansion basis functions which are eigenfunctions of the total angular momentum, J, because the coupled equations (see Section 3.D) are then diagonal in J and independent of its projection, M, on the space-fixed axis. The appropriate combination is

$$\begin{aligned}\Omega^{JM}_{j_1\tau_1 j_2 j\ell}&(\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma) \\ &= \sum_{\mu} <j\mu\ell m|JM> w^{j,\mu}_{j_1,\tau_1,j_2}(\Theta,\Phi,\alpha,\beta,\gamma) Y_{\ell m}(\Theta',\Phi') \\ &= \sum_{\mu} <j\mu\ell m|JM> <j_1 m_1 j_2 m_2|j\mu> W^{j_1}_{\tau_1,m_1}(\alpha\beta\gamma) Y_{j_2 m_2}(\Theta,\Phi) Y_{\ell m}(\Theta',\Phi')\end{aligned} \tag{4}$$

Here $<j_1 m_1 j_2 m_2|j_{12} m_{12}>$ is a Clebsch-Gordan angular momentum coupling coefficient and the sums are over the projection quantum numbers. We have first coupled the two rotor momenta, j_1 and j_2, to give a resultant, j, and then coupled j with the collision

orbital angular momentum, ℓ, to give J, the total momentum for the system.

C. Interaction potential

It is convenient to expand the interaction potential in a complete orthonormal set of angular functions. We choose complete sets of spherical harmonics for Θ,Φ and Θ',Φ' and rotation matrices for α,β,γ and we choose contracted products which are rotationally invariant:

$$V(R,\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma) = \sum v_{p_1q_1p_2p}(R)\ T_{p_1q_1p_2p}(\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)\ . \tag{5}$$

where

$$T_{p_1q_1p_2p}(\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma) = (1+\delta_{q_10})^{-1} \sum \begin{pmatrix} p_1 & p_2 & p \\ r_1 & r_2 & r \end{pmatrix} \tag{6}$$

$$Y_{p_2r_2}(\Theta'\Phi')\ Y_{pr}(\Theta\Phi)\ [\mathscr{D}^{p_1}_{q_1r_1}(\alpha,\beta,\gamma) + (-1)^{p_1+q_1+p_2+p}\ \mathscr{D}^{p_1}_{-q_1r_1}(\alpha,\beta,\gamma)]\ .$$

Here (:::) is a Wigner 3-j symbol, $\mathscr{D}^{p}_{qr}(\alpha,\beta,\gamma)$ is a Wigner rotation matrix and $Y_{pq}(\Theta\Phi)$ is a spherical harmonic, all as defined by Silver;[12] δ_{ij} is a Kronecker delta, equal to one if i=j and to zero otherwise; and the sum is over r_1, r_2, and r. Note that the phased sum over q_1 ensures that these functions are symmetric on reflection in the asymmetric rotor xz-plane.

Because of rotational invariance of the system as a whole, these functions can depend on only a smaller number of *relative* angles (sometimes called body-fixed angles, not to be confused with the rotor molecule body-fixed coordinate system discussed above). In general, one can choose three angles, corresponding to rotation of the collision system as a whole, in an arbitrary way. A convenient choice does this by fixing the asymmetric rotor orientation at α,β,γ=(0,0,0) and defining body-fixed θ,φ and θ',φ' as the collision direction and the linear molecule orientation *relative to the rotor molecule body-fixed axis system.* In terms of these relative coordinates Eqs. (5)-(6) can be written as

$$V(R,\theta,\varphi,\theta',\varphi') = \sum v_{p_1q_1p_2p}(R)\ t_{p_1q_1p_2p}(\theta,\varphi,\theta',\varphi')\ , \tag{7}$$

where

$$t_{p_1q_1p_2p}(\theta,\varphi,\theta',\varphi') = (1+\delta_{q_10})^{-1} \sum_{r_1 r_2 r} \begin{bmatrix} p_1 & p_2 & p \\ r_1 & r_2 & r \end{bmatrix} \quad (8)$$

$$Y_{p_2r_2}(\theta'\varphi') \; Y_{pr}(\theta\varphi) \; [\delta_{q_1r_1} + (-1)^{p_1+q_1+p_2+p} \; \delta_{-q_1r_1}] \; ,$$

and the sum is again over r_1,r_2,r.

D. Close coupling equations

The close coupling formalism for nonreactive molecular collision dynamics solves the time-independent Schrodinger equation by expanding the total system wavefunction in a basis which consists of the asymptotic vibration-rotation functions for the two colliding molecules and partial waves (spherical harmonics) for the angular part of the collision coordinate. This results in coupled second-order differential equations for functions of the collision distance. The coupling arises from the angle dependence of the intermolecular potential energy surface. With the expansion basis set described above the close coupled radial equations are

$$\left[d^2/dR^2 - \ell(\ell+1)/R^2 + k^2_{j_1\tau_1j_2}\right] F^{JM}_{\gamma\,\ell\leftarrow\gamma_I\ell}(R) = \quad (9)$$

$$(2m/\hbar^2) \sum_{\gamma'} < \Omega^{JM}_{\gamma} \; |V| \; \Omega^{JM}_{\gamma'} > F^{JM}_{\gamma'\,\ell'\leftarrow\gamma_I\ell}(R) \; ,$$

where γ stands for the set of rotor quantum numbers, j_1,τ_1,j_2,j, and the magnitude of the wavevector is defined by

$$k^2_{j_1\tau_1j_2} = (2m/\hbar^2) \; [E - \varepsilon_{j_1\tau_1} - \varepsilon_{j_2}] \; . \quad (10)$$

In Eq. (10) E is the total energy, $\varepsilon_{j_1\tau_1}$ and ε_{j_2} are energies of the asymmetric top and linear rotor, respectively, and m is the collision reduced mass.

With the interaction potential expanded as in Eqs. (5)-(8) the coupling matrix elements are

$$<\Omega^{JM}_{\gamma\,\ell} \; |V(R,\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)| \; \Omega^{JM}_{\gamma'\,\ell'}> = \sum_{p_1q_1p_2pkk'} v_{p_1q_1p_2p}(R) \quad (11)$$

$$(-1)^{J-j_1'+j_2'-j+k-p} \; (4\pi)^{-1} \; [j_1,j_1',j_2,j_2',j,j'.\ell,\ell',p_2,p]^{1/2}$$

$$\begin{Bmatrix} \ell & \ell' & p \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} j_2 & p_2 & j_2' \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} \ell & \ell' & p \\ j' & j & J \end{Bmatrix} \begin{Bmatrix} j_1' & j & p \\ j_1' & j_1 & p_1 \\ j_2 & j_2 & p_2 \end{Bmatrix} a^{j_1}_{\tau_1,k} a^{j_1'}_{\tau_1',k'}$$

$$[1+\delta_{q_1 0}]^{-1} \left[\begin{pmatrix} j_1 & p_1 & j_1' \\ -k & q_1 & k' \end{pmatrix} + (-1)^{p_1+q_1+p_2+p} \begin{pmatrix} j_1 & p_1 & j_1' \\ -k & -q_1 & k' \end{pmatrix} \right]$$

where $[a,b,...]=(2a+1)(2b+1)...$. There is no coupling between channel basis functions of differing total parity, $\mathcal{P} = \alpha_{j,\tau}\ \varepsilon_{j,\tau}\ (-1)^{J+j_1+j_2+\ell}$, as can readily be shown by noting that the coupling matrix elements are real and independent of the projection of the total momentum, M, and equating the complex conjugate of the matrix element with itself using

$$\Omega^{JM}_{j_1 \tau_1 j_2 j \ell}(\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)^* = (-1)^{j_1+j_2+\ell+J+M}\ \alpha_{j_1\tau_1}\ \varepsilon_{j_1\tau_1}\ \Omega^{J-M}_{j_1 \tau_1 j_2 j \ell}(\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma) \tag{12}$$

The coupled equations may thus be solved separately for each parity block.

The asymptotic behavior of the radial functions defines a scattering S-matrix. State-to-state cross sections are obtained from the S-matrices as

$$\sigma(j_1\tau_1 j_2 \rightarrow j_1'\tau_1' j_2') = \pi\ ([j_1,j_2]\ k^2_{j_1\tau_1 j_2})^{-1} \sum_{J \ell \ell' j j'} [J]\ |\delta_{\gamma\ell,\gamma'\ell'} - S^J_{\gamma\ell,\gamma'\ell'}|^2 \ . \tag{13}$$

E. Coupled states equations

The coupled states method may be obtained by transforming the radial scattering equations so that the centrifugal coupling is transferred from the potential coupling matrix on the right-hand side of Eq. (9) to the left-hand side, and then approximating this nondiagonal centrifugal term with an expression in which the off-diagonal terms are set to zero and in which the diagonal terms are approximated by a single, "effective" orbital angular momentum, λ, in all channels.[13] In general, λ is a function of ℓ and ℓ', the initial and final close coupling orbital angular momenta. However, especially simple cross section formulas result from either of the (unsymmetrical) choices $\lambda=\ell$ or $\lambda=\ell'$, i.e., either the initial or final channel orbital angular momentum, and virtually all

coupled states calculations have employed this choice, which is also adopted here.

The resulting coupled equations are formally similar to those of the close coupling method:

$$\left[d^2/dR^2 - \lambda(\lambda+1)/R^2 + k^2_{j_1\tau_1 j_2}\right] g^{\lambda\mu}_{\gamma\leftarrow\gamma_I}(R) = \tag{14}$$
$$(2m/\hbar^2) \sum_{\gamma'} < \Omega^{\lambda\mu}_{\gamma} |V| \Omega^{\lambda\mu}_{\gamma'} > g^{\lambda\mu}_{\gamma'\leftarrow\gamma_I}(R) \ .$$

Here $\lambda(\lambda+1)/R^2$ is the approximate centrifugal term. Thus, λ functions as an effective partial wave, while μ is the projection on the collision axis of the total rotor momentum, j. The coupling matrix elements are given by

$$<\Omega^{\lambda\mu}_{\gamma} |V(R,\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)| \Omega^{\lambda\mu}_{\gamma'}> = \sum_{p_1q_1p_2pkk'} v_{p_1q_1p_2p}(R) \tag{15}$$
$$(-1)^{j+j_1'+j_2'-\mu-k} (4\pi)^{-1} [j_1,j_1',j_2,j_2',j,j',p_2,p]^{1/2}$$
$$\begin{pmatrix} j_2 & p_2 & j_2' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & p & j' \\ \mu & 0 & -\mu \end{pmatrix} \begin{Bmatrix} j' & j & p \\ j_1' & j_1 & p_1 \\ j_2' & j_2 & p_2 \end{Bmatrix} a^{j_1}_{\tau_1,k} a^{j_1'}_{\tau_1',k'}$$
$$[1+\delta_{q_10}]^{-1} \left[\begin{pmatrix} j_1 & p_1 & j_1' \\ -k & q_1 & k' \end{pmatrix} + (-1)^{p_1+q_1+p_2+p} \begin{pmatrix} j_1 & p_1 & j_1' \\ -k & -q_1 & k' \end{pmatrix}\right]$$

Note that there is no coupling among different λ or μ values and that the coupling matrix elements are independent of λ.

The asymptotic behavior of the g(R) determines a coupled states scattering S-matrix in the same manner as for the close coupling method and state-to-state cross sections are given in terms of the S-matrices as

$$\sigma(j_1\tau_1 j_2 \rightarrow j_1'\tau_1' j_2') = \tag{16}$$
$$\pi \ ([j_1,j_2] \ k^2_{j_1\tau_1 j_2})^{-1} \sum_{\lambda\mu jj'} [\lambda] \ |\delta_{\gamma,\gamma'} - S^{\lambda\mu}_{\gamma,\gamma'}|^2 \ .$$

It is readily shown, using the properties of the channel basis functions under complex conjugation and the fact that the matrix elements are real, that changing the sign of μ results in

$$<\Omega^{\lambda-\mu}_{\gamma} |V(R,\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)| \Omega^{\lambda-\mu}_{\gamma'}> = (-1)^{j_1+j_2+j+j_1'+j_2'+j'} \tag{17}$$
$$\varepsilon_{j\tau} \ \alpha_{j\tau} \ \varepsilon_{j'\tau'} \ \alpha_{j'\tau'} \ <\Omega^{\lambda\mu}_{\gamma} |V(R,\Theta,\Phi,\Theta',\Phi',\alpha,\beta,\gamma)| \Omega^{\lambda\mu}_{\gamma'}>.$$

Since the potential coupling matrix elements for $-\mu$ differ from those for $+\mu$ by at most a phase which depends only on the rotor quantum numbers, the S-matrix elements can also differ by only a phase. For quantities which depend on the modulus of S-matrix elements and not on their phase, notably the state-to-state cross sections in Eq. (16), one needs to perform calculations only for nonnegative μ.

3. Calculations for H_2O - H_2

Calculation of the H_2O-H_2 potential and subsequent fit to 48 terms in the angular expansion, Eq. (7), have been described previously.[9] Using this fit we have done molecular scattering calculations with two major goals. First, we examine convergence of cross sections on increasing the size of the rotor basis set. Second, we test the accuracy of the coupled states approximation. The H_2O rotational functions and energy levels used here are the same as those described in Ref. 8. The H_2 rotational energies were calculated from the rotation constant, B=60.853 cm^{-1}. Calculations were done with the MOLSCAT[10] computer code; modifications needed to handle collisions of an asymmetric rigid rotor with a linear rigid rotor are implemented in version 14 of this code. We used the modified log-derivative method of Manolopoulos[14] to integrate the coupled equations. Tolerances were chosen to obtain inelastic cross sections accurate to at least 1% (or 0.01 $Å^2$ for small cross sections); the same criteria were used to truncate the sum over partial waves.

This collision system is particularly favorable for coupled channel methods since both species have large rotation constants with consequently few rotational levels accessible at thermal energies. Also, both species exist in para and ortho nuclear spin forms which are not interconverted by nonreactive collisions so that calculations can be done separately for the four possible para/ortho combinations. Nonetheless, to keep calculations tractable we have limited them to energies at which only the lowest H_2 level (j=0 for para-H_2 and j=1 for ortho-H_2) is accessible, i.e., no more than a few

hundred wavenumbers.

Results for para-H_2O in collisions with para-H_2 are given in Table 1 for total energies of 47, 100, and 300 cm^{-1} and for rotational basis sets of different size. The basis sets are labeled $B(n_1,n_2)$ which indicates that all H_2O functions with $j_1 \leq n_1$ (of the proper para or ortho symmetry) and all H_2 functions with $j_2 \leq n_2$ (only even j_2 for para-H_2 and odd j_2 for ortho-H_2) are included. Similar results for ortho-H_2O in collisions with para-H_2 are given in Table 2 and for para- and ortho-H_2O in collisions with ortho-H_2 in Tables 3 and 4, respectively. It might be noted that the largest close coupled calculations reported here, the B(5,3) basis results in Table 3, involved slightly over 700 coupled channels. In addition to accurate close coupling calculations, we have performed approximate coupled states calculations. These results are included in parentheses in Tables 1-4.

It can be seen that the B(4,n) bases give results which are in most cases within 10% of the B(5,n) results, even at energies where some $j_1=4$ channels are accessible. Convergence tends to be worse though for cross sections among levels near the basis set limit, as expected. For excitation by para-H_2, inclusion of $j_2=2$ channels is required for 10% accuracy even though these channels are not asymptotically accessible. For excitation by ortho-H_2, however, inclusion of $j_2=3$ channels is less important.

Examination of the tables shows that cross sections for transitions induced by ortho-H_2 are larger -- sometimes dramatically so -- than cross sections for the same transitions induced by collisions with para-H_2. This effect is readily seen by comparing the 100 cm^{-1} values from Table 1 with the values in Table 3 which are at the same collisional kinetic energy. This result is not surprising. At the energies considered here only the $j_2=0$ level is accessible in para-H_2 and, unlike for higher rotational levels, the $j_2=0$ level does not support a long-range dipole-quadrupole interaction, leading to greatly reduced cross sections. Excitation by warmer para-H_2, where $j_2=2$ is populated, is expected to lead to cross sections more similar to those found here for ortho-H_2.[15]

This reduction in rates for excitation by cold para-H_2 has also been observed experimentally by Oka[16] and in earlier theoretical results for NH_3-H_2 collisions.[3,4]

We find that the coupled states approximation does not predict quantitatively reliable cross sections, especially at the lowest energies, although it generally gives the correct hierarchy of values. The approximation is expected to become more accurate at higher collision energies and, indeed, for para-H_2 collisions it is generally reliable to 10-20% except at the lowest energies and for some of the small cross sections. Not surprisingly, this accuracy is consistent with that found for H_2O-He.[7,8] The coupled states approximation is significantly less accurate for ortho-H_2 collisions which is believed to reflect the greater anisotropy and long-range nature of the potential in this case.

Because collisional excitation rates for H_2O-H_2 have not been available, astrophysical applications[6] have relied on rates computed for H_2O-He. The rationale for this procedure is that para-H_2 in its ground rotational state is analogous to a structureless atom and should have collision cross sections similar to those for He, perhaps multiplied by a small scaling factor to account for the smaller reduced mass and somewhat larger size of H_2 as compared with He. The validity of this procedure is examined in Table 5 which compares coupled states cross sections for excitation of para-H_2O by para-H_2 with values computed for H_2O-He[17] at a total energy of 300 cm^{-1}. It can be seen on the one hand that a simple multiplicative scaling relation is not quantitatively accurate. On the other hand, the H_2 cross sections are the same order of magnitude as the He cross sections and, with a few exceptions, both show the same hierarchy of values as a function of final state for a given initial state. A similar comparison is made in Table 6 between cross sections for ortho-H_2O calculated here and values for excitation by He obtained from an earlier theoretical potential.[18]

4. Conclusions

We have performed close coupling calculations for H_2O-H_2 in which we have varied the size of the rotor basis sets. We find that cross sections converged to a few percent can be achieved by including only a few closed rotational states of H_2O. For excitation by para-H_2 in its lowest, j_2=0 level, it is necessary to include j_2=2 basis functions to obtain better than 10% precision. Although the results are not shown in the tables, we also considered (within the coupled states approximation) the effect of including j_2=4 basis functions, finding them to have an insignificant effect. Inclusion of closed H_2 rotational states seems less important for excitation by ortho-H_2.

The coupled states approximation, which has proved useful for studies of excitation by He atoms, is found here to be somewhat less reliable for excitation by H_2, although it may prove to be adequate at higher collision energies. It will be worthwhile to consider other approximate methods, for example, the decoupled L-dominant method[19] which is expected to be better for systems with strong long-range forces.

We have examined the common practice of adapting rates of excitation by He atoms to mimic excitation by para-H_2 in its lowest, j_2=0, level, finding that this is qualitatively reasonable but certainly not quantitatively accurate. We have also examined the expectation that cross sections for excitation by ortho-H_2 are significantly larger than those for excitation by cold para-H_2 and have found this to be true; in some cases the enhancement is much more than the factor of 2-4 which has been generally assumed on the basis of simple arguments.[15]

We plan to extend the calculations reported here to obtain rates for excitation of H_2O by H_2 which are needed to interpret astrophysical observations. On the basis of results presented here we expect that it will be possible, though expensive, to obtain accurate H_2 excitation rates among the lower H_2O levels at temperatures to a few hundred kelvin with current computational capabilities. These will be quite useful, for example, for interpreting planned observations of the $1_{1,0}$-$1_{0,1}$ transition of interstellar

water with the Submillimeter Wave Astronomy Satellite. Unfortunately, calculation of rates among the high-lying rotational levels levels and for the high kinetic temperatures (to about 1000 K) required for a proper understanding of observed interstellar masers are not currently feasible using the accurate close coupling method. Calculation of rates for these transitions and temperatures will require a judicious choice of approximate approaches as well as enormous computational power.

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Table 1. Cross sections for para-H_2O in collisions with para-H_2 as a function of basis set size; the notation B(n_1,n_2) indicates H_2O functions with $j_1 \le n_1$ and H_2 functions with $j_2 \le n_2$. Values from the coupled states approximation are listed in parentheses. The collision energy is given in cm^{-1} and cross sections are in $Å^2$.

Energy	initial	final	B(5,2)	B(5,0)	B(4,2)
47.0	$0_{0,0}$	$1_{1,1}$	2.91 (1.59)	2.41 (1.48)	3.16 (1.57)
100.0	$0_{0,0}$	$1_{1,1}$	2.83 (2.48)	2.25 (1.93)	2.81 (2.47)
		$2_{0,2}$	3.75 (3.34)	2.65 (2.28)	3.70 (3.30)
		$2_{1,1}$	0.002 a	0.001 a	0.002 a
	$1_{1,1}$	$2_{0,2}$	1.16 (0.66)	0.87 (0.44)	1.16 (0.65)
		$2_{1,1}$	1.75 (1.55)	1.30 (1.13)	1.74 (1.53)
	$2_{0,2}$	$2_{1,1}$	0.45 (0.44)	0.19 (0.20)	0.45 (0.45)
300.0	$0_{0,0}$	$1_{1,1}$	4.53 (4.46)	4.23 (4.18)	4.53 (4.46)
		$2_{0,2}$	2.97 (3.13)	1.99 (2.05)	2.97 (3.11)
		$2_{1,1}$	0.02 a	0.01 a	0.02 a
		$2_{2,0}$	0.55 (0.36)	0.38 (0.24)	0.55 (0.36)
		$3_{1,3}$	0.75 (0.84)	1.40 (1.60)	0.75 (0.85)
		$3_{2,2}$	0.001 a	0.001 a	0.001 a
		$4_{0,4}$	0.05 (0.05)	0.08 (0.09)	0.05 (0.05)
		$4_{1,3}$	0.001 a	0.001 a	0.001 a
		$3_{3,1}$	0.003 (0.002)	0.005 (0.005)	0.003 (0.002)
	$1_{1,1}$	$2_{0,2}$	1.50 (1.58)	1.61 (1.63)	1.52 (1.59)
		$2_{1,1}$	3.98 (3.98)	2.86 (2.86)	3.97 (3.97)
		$2_{2,0}$	1.43 (1.46)	1.39 (1.42)	1.44 (1.47)
		$3_{1,3}$	0.68 (0.64)	0.46 (0.42)	0.64 (0.60)
		$3_{2,2}$	0.14 (0.16)	0.23 (0.25)	0.14 (0.15)
		$4_{0,4}$	0.24 (0.28)	0.41 (0.42)	0.23 (0.25)
		$4_{1,3}$	0.002 (0.000)	0.003 (0.002)	0.002 (0.000)
		$3_{3,1}$	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)

$^3_{2,2}$	$^4_{0,4}$	0.12	(0.14)	0.04	(0.05)	0.12	(0.16)
	$^4_{1,3}$	0.64	(0.62)	0.39	(0.44)	0.46	(0.43)
	$^3_{3,1}$	0.71	(0.47)	0.40	(0.53)	0.67	(0.48)
$^4_{0,4}$	$^4_{1,3}$	0.68	(0.57)	0.37	(0.35)	0.67	(0.61)
	$^3_{3,1}$	0.04	(0.03)	0.03	(0.04)	0.03	(0.03)
$^4_{1,3}$	$^3_{3,1}$	0.14	(0.18)	0.06	(0.19)	0.22	(0.31)

a. These cross sections are identically zero in the coupled states approximation.

Table 2. Cross sections for ortho-H_2O in collisions with para-H_2 as a function of basis set size. Values from the coupled states approximation are listed in parentheses. The collision energy is given in cm^{-1} and cross sections are in $Å^2$.

Energy	initial	final	B(5,2)	B(5,0)	B(4,2)
123.79	$1_{0,1}$	$1_{1,0}$	1.62 (1.52)	1.46 (1.65)	1.60 (1.50)
		$2_{1,2}$	1.94 (1.64)	1.67 (1.83)	1.94 (1.67)
	$1_{1,0}$	$2_{1,2}$	2.03 (2.09)	1.73 (1.98)	1.94 (2.06)
300.0	$1_{0,1}$	$1_{1,0}$	2.27 (2.26)	2.12 (2.13)	2.28 (2.28)
		$2_{1,2}$	2.51 (2.43)	2.55 (2.47)	2.51 (2.43)
		$2_{2,1}$	0.47 (0.32)	0.34 (0.22)	0.48 (0.33)
		$3_{0,3}$	0.96 (0.87)	0.60 (0.50)	0.89 (0.80)
		$3_{1,2}$	0.04 (0.04)	0.08 (0.09)	0.04 (0.04)
		$3_{2,1}$	0.08 (0.06)	0.07 (0.06)	0.07 (0.05)
		$3_{3,0}$	0.003 (0.005)	0.003 (0.003)	0.002 (0.001)
		$4_{1,4}$	0.29 (0.30)	0.47 (0.48)	0.27 (0.29)
	$3_{0,3}$	$3_{1,2}$	1.16 (1.12)	0.96 (0.87)	1.17 (1.12)
		$3_{2,1}$	0.15 (0.14)	0.10 (0.07)	0.15 (0.12)
		$3_{3,0}$	0.03 (0.02)	0.02 (0.02)	0.02 (0.02)
		$4_{1,4}$	1.75 (1.81)	1.25 (1.28)	1.35 (1.39)
	$3_{1,2}$	$3_{2,1}$	1.10 (1.17)	0.80 (0.74)	1.13 (1.07)
		$3_{3,0}$	0.16 (0.52)	0.01 (0.01)	0.04 (0.04)
		$4_{1,4}$	0.21 (0.21)	0.09 (0.10)	0.04 (0.03)
	$3_{2,1}$	$3_{3,0}$	0.77 (0.55)	0.40 (0.47)	0.70 (0.54)
		$4_{1,4}$	0.36 (0.48)	0.21 (0.25)	0.20 (0.26)
	$3_{3,0}$	$4_{1,4}$	0.49 (0.13)	0.09 (0.06)	0.42 (0.14)

Table 3. Cross sections for para-H_2O in collisions with ortho-H_2 as a function of basis set size. Values from the coupled states approximation are listed in parentheses. The collision energy is given in cm^{-1} and cross sections are in $Å^2$.

Energy	initial	final	B(5,3)		B(5,1)		B(4,3)	
221.71	$0_{0,0}$	$1_{1,1}$	28.61	(16.34)	28.95	(16.26)	28.65	(16.37)
		$2_{0,2}$	7.15	(5.59)	6.42	(4.94)	7.07	(5.52)
		$2_{1,1}$	0.45	(0.34)	0.41	(0.29)	0.45	(0.34)
	$1_{1,1}$	$2_{0,2}$	23.14	(14.22)	22.82	(13.84)	23.08	(14.17)
		$2_{1,1}$	3.49	(2.48)	3.41	(2.35)	3.48	(2.46)
	$2_{0,2}$	$2_{1,1}$	10.55	(7.54)	10.82	(7.70)	10.58	(7.56)

Table 4. Cross sections for ortho-H_2O in collisions with ortho-H_2 as a function of basis set size. Values from the coupled states approximation are listed in parentheses. The collision energy is given in cm^{-1} and cross sections are in $Å^2$.

Energy	initial	final	B(5,3)	B(5,1)		B(4,1)	
421.71	$1_{0,1}$	$1_{1,0}$	(19.45)	12.37	(19.39)	12.40	(19.43)
		$2_{1,2}$	(7.70)	11.83	(7.67)	11.76	(7.59)
		$2_{2,1}$	(1.76)	2.36	(1.70)	2.34	(1.68)
		$3_{0,3}$	(1.85)	2.74	(1.65)	2.72	(1.62)
		$3_{1,2}$	(0.45)	0.46	(0.43)	0.44	(0.41)
		$3_{2,1}$	(0.24)	0.42	(0.25)	0.42	(0.25)
		$3_{3,0}$	(0.02)	0.03	(0.03)	0.03	(0.03)
		$4_{1,4}$	(0.29)	0.32	(0.34)	0.29	(0.31)
	$3_{0,3}$	$3_{1,2}$	(9.58)	11.88	(9.65)	11.97	(9.75)
		$3_{2,1}$	(1.23)	1.30	(1.17)	1.42	(1.32)
		$3_{3,0}$	(0.08)	0.08	(0.10)	0.10	(0.08)
		$4_{1,4}$	(2.67)	4.61	(2.60)	3.68	(1.68)
	$3_{1,2}$	$3_{2,1}$	(8.76)	13.84	(8.67)	13.79	(8.62)
		$3_{3,0}$	(0.35)	0.28	(0.39)	0.27	(0.41)
		$4_{1,4}$	(2.09)	2.42	(2.01)	2.21	(1.79)
	$3_{2,1}$	$3_{2,0}$	(1.64)	1.84	(1.46)	1.83	(1.37)
		$4_{1,4}$	(2.45)	1.98	(2.54)	1.85	(2.61)
	$3_{2,0}$	$4_{1,4}$	(2.42)	2.65	(3.40)	2.78	(2.22)

Table 5. Comparison of coupled states collision cross sections, in $Å^2$, for para-H_2O excited by He atoms and by para-H_2 at an energy of 300 cm^{-1}.

initial	final	He [a]	para-H_2
$0_{0,0}$	$1_{1,1}$	3.82	4.46
	$2_{0,2}$	1.05	3.13
	$2_{2,0}$	0.13	0.36
	$3_{1,3}$	1.36	0.84
	$4_{0,4}$	0.09	0.05
	$3_{3,1}$	0.002	0.002
$1_{1,1}$	$2_{0,2}$	1.68	1.58
	$2_{1,1}$	1.05	3.98
	$2_{2,0}$	1.09	1.46
	$3_{1,3}$	0.25	0.64
	$3_{2,2}$	0.14	0.16
	$4_{0,4}$	0.19	0.28
	$4_{1,3}$	0.0008	0.0005
	$3_{3,1}$	0.004	0.01
$2_{0,2}$	$2_{1,1}$	1.55	1.80
	$2_{2,0}$	0.06	0.16
	$3_{1,3}$	1.35	1.78
	$3_{2,2}$	0.08	0.19
	$4_{0,4}$	0.02	0.30
	$4_{1,3}$	0.006	0.01
	$3_{3,1}$	0.0009	0.004

a. Values from Ref. 17.

Table 6. Comparison of coupled states collision cross sections, in $Å^2$, for ortho-H_2O excited by He atoms and by para-H_2 at an energy of 300 cm^{-1}.

initial	final	He [a]	para-H_2
$1_{0,1}$	$1_{1,0}$	0.79	2.26
	$2_{1,2}$	2.62	2.43
	$2_{2,1}$	0.32	0.32
	$3_{0,3}$	0.53	0.87
	$3_{1,2}$	0.15	0.04
	$3_{2,1}$	0.31	0.06
	$3_{3,0}$	0.01	0.005
$1_{1,0}$	$2_{1,2}$	0.32	1.17
	$2_{2,1}$	1.34	1.85
	$3_{0,3}$	2.34	0.40
	$3_{1,2}$	0.59	0.68
	$3_{2,1}$	0.06	0.04
	$3_{3,0}$	0.05	0.04
$2_{1,2}$	$2_{2,1}$	0.52	0.60
	$3_{0,3}$	0.75	1.50
	$3_{1,2}$	0.70	1.23
	$3_{2,1}$	0.96	0.48
	$3_{3,0}$	0.03	0.02
$2_{2,1}$	$3_{0,3}$	0.44	0.16
	$3_{1,2}$	1.52	0.62
	$3_{2,1}$	0.85	1.66
	$3_{3,0}$	0.52	0.50

a. Values from Ref. 18.